

# A simple method for the Kramers-Kronig analysis of reflectance spectra measured with diamond anvil cell

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**Abstract.** When the optical reflectance spectrum of a sample under high pressure is studied with a diamond anvil cell, it is measured at a sample/diamond interface. Due to the large refractive index of diamond, the resulting reflectance  $R_d(\omega)$  may substantially differ from that measured in vacuum. To obtain optical constants from  $R_d(\omega)$ , therefore, the usual Kramers-Kronig (KK) analysis cannot be straightforwardly applied, and either a spectral fitting or a modified KK transform has been used. Here we describe an alternative method to perform KK analysis on  $R_d(\omega)$ . This method relies on the usual KK transform with an appropriate cutoff and extrapolation to  $R_d(\omega)$ , and may offer a simpler approach to obtain infrared conductivity from measured  $R_d(\omega)$ .

## 1. Introduction

Infrared (IR) spectroscopy has been a powerful tool to study the microscopic carrier dynamics and electronic structures in strongly correlated electron materials, such as rare earth ( $f$  electron), transition metal ( $d$  electron), and organic ( $p$  electron) compounds [1]. The IR spectroscopy technique has been also performed under high pressure using a diamond anvil cell (DAC) [2-13] since the strongly correlated materials show many interesting physical properties under high pressure. In a DAC, a pair of diamond anvils and a thin metal gasket are used to seal a sample and a pressure transmitting medium [6]. A typical diameter of the diamond surface is 0.8 mm to reach a pressure of 10 GPa, and 0.6 mm to reach 20 GPa. Therefore the sample in this experiment should have dimensions of the order of 100  $\mu\text{m}$ . To perform an infrared (IR) reflectance study on such a small sample under the restricted sample space in a DAC, synchrotron radiation (SR) has been used as a bright source of both far and mid-infrared. In fact, high pressure IR spectroscopy with DAC is currently one of the major applications of IR-SR [4-7,9-13].

With a DAC, the reflectance is measured between the sample/diamond interface, in contrast to the usual case of sample/vacuum or sample/air interface. The normal-incidence reflectance of a sample relative to a transparent medium of (real) refractive index  $n_0$  is given by the Fresnel's formula as [14, 15]:

$$R(\omega) = \frac{(n - n_0)^2 + k^2}{(n + n_0)^2 + k^2}. \quad (1)$$

Here,  $\hat{n} = n + ik$  is the complex refractive index of the sample, and  $n_0=2.4$  for diamond and 1.0 for vacuum. Hereafter, we denote  $R(\omega)$  at sample/diamond interface as  $R_d(\omega)$ , and that at sample/vacuum interface as  $R_0(\omega)$ . From Eq. (1), it is easily seen that  $R_d(\omega)$  of a sample measured in DAC may be substantially different from  $R_0(\omega)$ .

The purpose of this study is to consider the Kramers-Kronig (KK) analysis of  $R_d(\omega)$  data measured in DAC. KK analysis has been widely used to derive optical constants such as the refractive index, dielectric function and optical conductivity from a measured  $R_0(\omega)$  spectrum [14, 15]. However, due to the difference between  $R_0(\omega)$  and  $R_d(\omega)$  discussed above, the usual KK analysis method cannot be straightforwardly applied to  $R_d(\omega)$  [16]. To derive optical constants from  $R_d(\omega)$ , therefore, previous high pressure IR studies used either a Drude-Lorentz spectral fitting [2, 5, 6, 7, 9, 11, 12] or a modified KK transform [3, 8, 10, 13]. In this work, we propose a different method, which relies on the usual KK transform with an appropriate cutoff to the  $R_d(\omega)$ , as an alternative approach to obtain the infrared  $\sigma(\omega)$  from  $R_d(\omega)$ . The validity of the proposed method is demonstrated with actually measured reflectance data of  $\text{PrRu}_4\text{P}_{12}$ .

## 2. Kramers-Kronig analysis of reflectance spectra

The complex reflectivity of the electric field,  $\hat{r}$ , is expressed as [14, 15]

$$\hat{r}(\omega) = \frac{n_0 - \hat{n}(\omega)}{n_0 + \hat{n}(\omega)} = r(\omega)e^{i\theta(\omega)}. \quad (2)$$

Here  $r(\omega)$  is the square root of the reflectance  $R(\omega)$ , which is actually measured in experiments. Then the real and imaginary parts of  $\hat{n}$  can be expressed in terms of  $r$  and  $\theta$  as

$$n = \frac{1 - r^2}{1 + r^2 + 2r \cos \theta} \cdot n_0 \quad (3)$$

and

$$k = \frac{-2r \sin \theta}{1 + r^2 + 2r \cos \theta} \cdot n_0, \quad (4)$$

respectively. Therefore, if  $\theta(\omega)$  can be derived from measured  $r(\omega)$  with KK analysis even for the sample/diamond reflection case,  $n(\omega)$  and  $k(\omega)$  can also be derived simply by setting  $n_0=2.4$  in Eqs. (2) and (3). Then, the imaginary part of the complex dielectric function is given as  $\epsilon_2 = 2n(\omega)k(\omega)$ , and the optical conductivity is given as  $\sigma(\omega) = \frac{\omega}{4\pi}\epsilon_2(\omega)$  [14, 15].

In performing KK analysis on reflectance data, usually the logarithm of  $\hat{r}$ , namely

$$\ln \hat{r}(\omega) = \ln r(\omega) + i\theta(\omega) \quad (5)$$

is regarded as a complex response function. In the case of sample/vacuum reflection, the KK relation between  $\ln r(\omega)$  and  $\theta(\omega)$  is expressed as [14, 15]

$$\theta(\omega) = -\frac{2\omega}{\pi}P \int_0^\infty \frac{\ln r(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (6)$$

Here,  $P$  denotes the principal value. In deriving this relation, it is required that  $\ln \hat{r}(\hat{\omega})$  has no poles in the upper complex  $\hat{\omega}$  plane when  $|\omega|$  is finite. This is correct since  $r(\omega) \rightarrow 0$  only when  $\omega \rightarrow \infty$  in the case of  $n_0=1$ . However, when  $n_0 > 1$  as in the case of sample/diamond interface,  $\hat{n} = n_0$  may be satisfied at some point on the upper imaginary axis [16]. This point is denoted as  $\hat{\omega} = i\beta$ , where  $\beta$  is a real, positive and finite number. When  $\hat{n} = n_0$ ,  $\hat{r} = 0$  from Eq. (2) and  $\ln \hat{r}$  therefore has a pole at  $\hat{\omega} = i\beta$ . Accordingly, the KK relation in this case must be modified to [16]

$$\theta(\omega) = -\frac{2\omega}{\pi}P \int_0^\infty \frac{\ln r(\omega')}{\omega'^2 - \omega^2} d\omega' + [\pi - 2 \arctan(\beta/\omega)]. \quad (7)$$

Namely, the presence of a medium with  $n_0 > 1$  brings an extra phase shift, indicated by the square bracket in Eq. (7), into the KK relation. Note that the extra phase shift is a decreasing

function of  $\beta/\omega$ , and that the original KK relation of Eq. (6) is recovered when  $\beta/\omega \rightarrow \infty$  [16]. Detailed theoretical considerations on the extra phase shift in various situations have been reported [17, 18]. In the case of actual experimental studies, however, the precise value of  $\beta$  may not be known. Accordingly, the value of  $\beta$  has been estimated from experimental  $R_d(\omega)$  data by use of a combination of DL fitting and the modified KK transform [3, 8, 10, 13]. In this method, one uses Eq. (7) with  $r(\omega) = \sqrt{R_d(\omega)}$  and looks for a value of  $\beta$  that well reproduces the  $\sigma(\omega)$  given by a DL fitting of  $R_d(\omega)$ .

Note that, on the other hand, if the frequency range of interest is lower than the value of  $\beta$ , effects of the extra phase may be only minor, and the usual KK transform of Eq. (6), combined with the use of  $n_0=2.4$  in Eqs. (3) and (4), might give sufficiently accurate values of optical constants. We will examine the validity of such a procedure in the next section.

### 3. Simulation with measured reflectance spectra

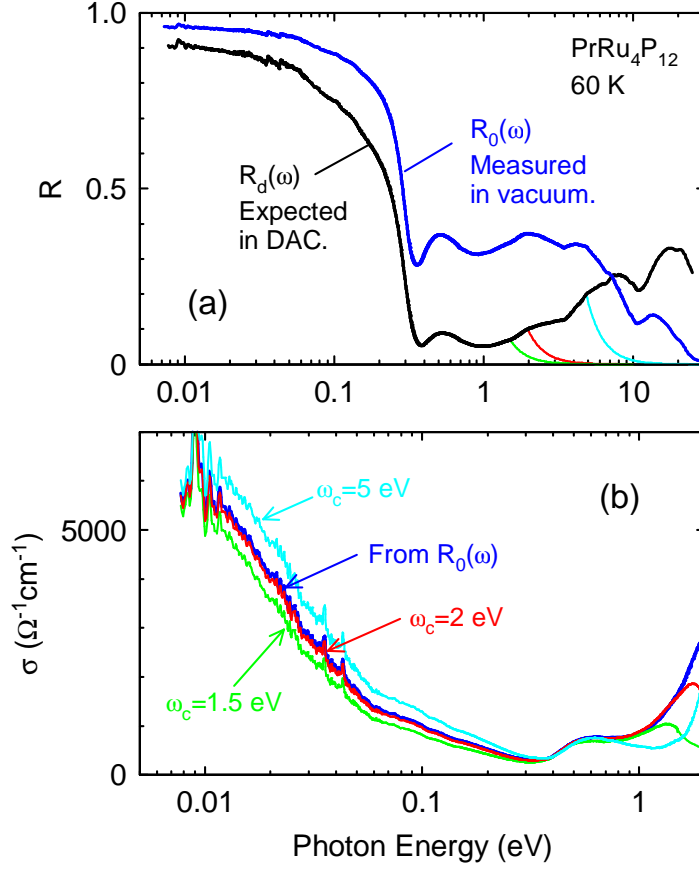
Here, we use  $R_0(\omega)$  spectra actually measured on  $\text{PrRu}_4\text{P}_{12}$  [19]. This compound is well known for showing a metal-to-insulator transition at about 60 K [20], and a clear energy gap in  $\sigma(\omega)$  was observed in our previous work [19]. Here we use  $R_0(\omega)$  at 60 K (metal) and 9 K (insulator) measured over a wide photon energy range of 0.008-30 eV [19], which are shown by the blue curve in Figs. 1(a) and 2(a). The procedure is the following.

- (i) The full  $R_0(\omega)$  spectrum is KK analyzed with Eq. (6) to obtain  $n(\omega)$ ,  $k(\omega)$  and  $\sigma(\omega)$ .
- (ii) The above  $n(\omega)$  and  $k(\omega)$  are substituted into Eq. (1) with  $n_0=2.4$  to derive  $R_d(\omega)$  that is *expected* in a DAC.
- (iii) The  $R_d(\omega)$  obtained above is used with the usual KK transform of Eq. (6) and  $n_0=2.4$  in Eqs. (3) and (4), to obtain  $n(\omega)$ ,  $k(\omega)$  and  $\sigma(\omega)$ . Before this is done, an appropriate cutoff and extrapolation are made to the  $R_d(\omega)$ , as described in detail below.

If the KK analysis on  $R_d(\omega)$  works properly, the resulting  $\sigma(\omega)$  from (iii) should well agree with that given by  $R_0(\omega)$  and the usual KK analysis.

We first examine the 60 K data. The expected  $R_d(\omega)$  at 60 K obtained by (i) and (ii) is indicated by the black curve in Fig. 1(a). In carrying out the integration in Eq. (6), the  $R_0(\omega)$  spectrum were extrapolated below 0.008 eV and above 30 eV with the Hagen-Rubens and  $\omega^{-4}$  functions, respectively. It is seen in Fig. 1(a) that  $R_d(\omega)$  shows very high values above about 4 eV. This physically unrealistic feature resulted from the unphysical assumption of constant  $n_0=2.4$  in the entire spectral range. In reality, of course, the refractive index of diamond cannot be constant and real near and above the band gap, where it shows strong light absorption. In addition, when  $\omega \rightarrow \infty$ ,  $n(\omega) \rightarrow 1$  and  $k(\omega) \rightarrow 0$ , and therefore  $R_d(\omega) \rightarrow 0$  must hold just like any other material. Accordingly, before performing KK transform in (iii),  $R_d(\omega)$  in Fig. 1(a) was cut off at some energy  $\omega_c$ , and then it was extrapolated with  $\omega^{-4}$  function. Several different values of  $\omega_c$  were tried, as shown in Fig. 1(a). For each value of  $\omega_c$ , the usual KK transform of Eq. (6) was made to get  $\theta(\omega)$ , which was then used to derive  $n(\omega)$  and  $k(\omega)$  with  $n_0=2.4$  in Eqs. (3) and (4), and to finally obtain  $\sigma(\omega)$ .

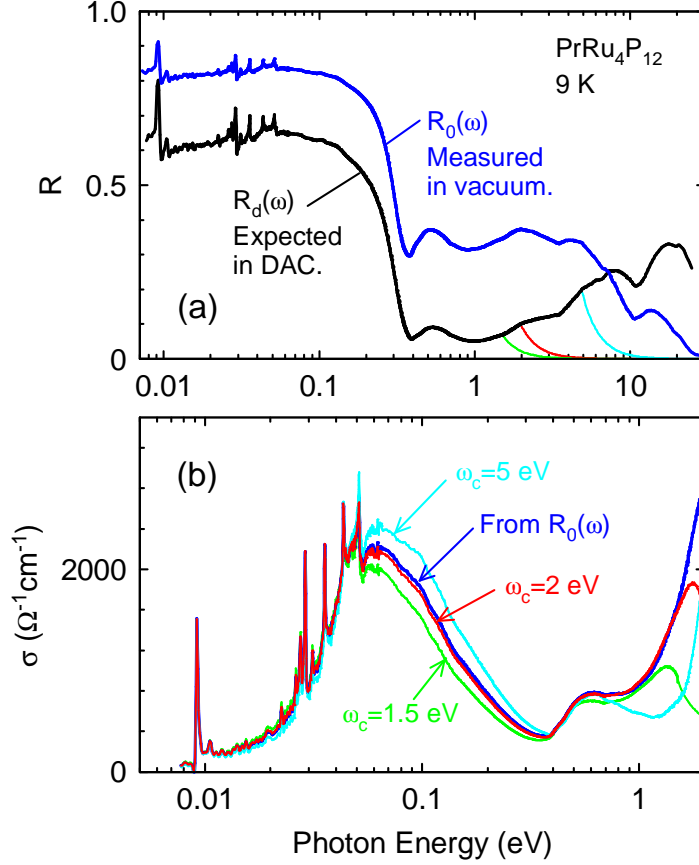
Figure 1(b) shows the  $\sigma(\omega)$  spectra obtained as described above, with different values of  $\omega_c$  which are also indicated in Fig. 1(a). It is seen that the obtained  $\sigma(\omega)$  spectra strongly depend on  $\omega_c$ . With  $\omega_c=2.0$  eV, the resulting  $\sigma(\omega)$  below 1.5 eV agrees very well with that derived from the original  $R_0(\omega)$ . (Actually,  $\omega_c=2.2$  eV gives the best agreement, but  $\omega_c=2.0$  eV data is shown instead. This is because the 2.2 eV data almost completely overlaps with that from  $R_0(\omega)$ , making it difficult to distinguish them in the figure.) The result for the 9 K data, where the sample is an insulator (semiconductor), is also shown in Fig. 2. A good agreement is again observed between the  $\sigma(\omega)$  derived from the full  $R_0(\omega)$  and that from  $R_d(\omega)$  with  $\omega_c=2$  eV. The spectral range of their good agreement is below 1.5 eV, which is similar to the case of 60 K data discussed above. Note also that both 9 K and 60 K data show good agreement with the



**Figure 1.** (a)  $R_0(\omega)$  is the reflectance spectrum of  $\text{PrRu}_4\text{P}_{12}$  measured at 60 K in vacuum [19], and  $R_d(\omega)$  is that expected in a DAC calculated from  $R_0(\omega)$  as described in the text. The green, red, and light blue curves are  $\omega^{-4}$  extrapolations with cutoff energies of  $\omega_c=1.5$ , 2, and 5 eV, respectively. (b) The optical conductivity ( $\sigma$ ) obtained with KK analysis of  $R_0(\omega)$  is compared with those obtained with KK analysis of  $R_d(\omega)$  with a cutoff at  $\omega_c=1.5$ , 2, and 5 eV, and  $\omega^{-4}$  extrapolations above them. Below 1.5 eV,  $\sigma(\omega)$  obtained from  $R_d(\omega)$  with  $\omega_c=2$  eV agrees very well with that obtained from  $R_0(\omega)$ .

common value of  $\omega_c=2$  eV. These results show that, for any spectral change in  $R_d(\omega)$  (either temperature- or pressure-induced) below 1.5 eV, the corresponding  $\sigma(\omega)$  can be obtained by the present method. In actual high pressure studies of strongly correlated materials with DAC [2-13],  $R_d(\omega)$  is usually measured below 1-2 eV. Hence, above the high energy limit of  $R_d(\omega)$  measurement, the  $R_d(\omega)$  expected from  $R_0(\omega)$  can be connected to the measured  $R_d(\omega)$ , with the cutoff and extrapolation discussed above. Then the connected  $R_d(\omega)$  may be KK transformed to obtain  $\sigma(\omega)$ , as discussed above. An obvious condition required for this method to work properly is that the pressure- and temperature-induced changes of  $R_d(\omega)$  should be limited below certain energy, which is 1.5 eV for  $\text{PrRu}_4\text{P}_{12}$  as seen in Figs. 1(b) and 2(b). This condition is actually met in the high pressure data of  $\text{PrRu}_4\text{P}_{12}$ , which has enabled us to derive its  $\sigma(\omega)$  under pressure up to 14 GPa using the present method [21].

We have also done similar simulations for other compounds, both metals and insulators, using actually measured data, and have obtained similar results. Namely, when an appropriate cutoff and extrapolation are applied to  $R_d(\omega)$ , the usual KK transform of Eq. (6) gave  $\sigma(\omega)$



**Figure 2.** (a)  $R_0(\omega)$  is the reflectance spectrum of  $\text{PrRu}_4\text{P}_{12}$  measured at 9 K in vacuum [19], and  $R_d(\omega)$  is that expected in a DAC calculated from  $R_0(\omega)$  as described in the text. The green, red, and light blue curves are  $\omega^{-4}$  extrapolations with cutoff energies of  $\omega_c=1.5$ , 2, and 5 eV, respectively. (b) The optical conductivity ( $\sigma$ ) obtained with KK analysis of  $R_0(\omega)$  is compared with those obtained with KK analysis of  $R_d(\omega)$  with a cutoff at  $\omega_c=1.5$ , 2, and 5 eV, and  $\omega^{-4}$  extrapolations above them.

spectra which agreed very well with those directly obtained from the wide range  $R_0(\omega)$ . A limitation of the present method is, as already mentioned above, it can give correct  $\sigma(\omega)$  only below certain photon energy (1.5 eV in the case of  $\text{PrRu}_4\text{P}_{12}$ ). Hence this method is useful when the temperature and pressure dependences of  $R_d(\omega)$  is limited to below certain energy. In addition, to use the present method, it is required that  $R_0(\omega)$  is known over a wide enough photon energy range, since  $n(\omega)$  and  $k(\omega)$  must be obtained from  $R_0(\omega)$  with the usual KK analysis. While a mathematically rigorous justification of the proposed method is beyond the scope of this work, this method may be very useful as a simple analysis technique of reflectance spectra measured under high pressure with DAC.

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